

(54) (Title of the Invention)

Stone-like artificial marble

(57) (Abstract)

(Object)

An object is to provide stone-like artificial marble excellent in heat crack resistance

(Constitution)

Stone-like artificial marble obtained by polymerization-hardening a composition comprising a methyl methacrylate partial polymer syrup (A) in an amount of 20 to 50% by weight based on the composition, a cross-linkable vinyl monomer (B) in an amount of 0.01 to 10% by weight based on (A), and at least one inorganic filler (C) selected from aluminum hydroxide, magnesium hydroxide, calcium carbonate and silica and crushed particles (D) obtained by crushing a resin containing inorganic fillers for coloration in the same composition as in the case of execution of the present invention having an average particle size of 0.24 to 2.8 mm and containing substantially no particles having a particle size of less than 0.1 mm and particles having a particle size of over 5 mm, in an amount of 5 to 25% by weight based on the whole composition, wherein the total amount of inorganic fillers in the component (C) and the component (D) is 30 to 70% by weight.

(Claims)

1. Stone-like artificial marble obtained by polymerization-hardening a composition comprising methyl methacrylate or a monomer mixture of methyl methacrylate as the main component with other vinyl monomer having one vinyl group in the molecule or its partial polymer syrup (A) in an amount of 20 to 50% by weight based on the whole composition, a cross-linkable vinyl monomer having two or more vinyl groups in the molecule (B) in an amount of 0.01 to 10% by weight based on (A), and at least one inorganic filler (C) selected from aluminum hydroxide, magnesium hydroxide, calcium carbonate and silica and crushed particles (D) having an average particle size of 0.24 to 2.8 mm and containing substantially no particles having a particle size of less than 0.1 mm and particles having a particle size of over 5 mm, in an amount of 5 to 25% by weight based on the whole composition, wherein the total amount of inorganic fillers in the component (C) and the component (D) is 30 to 70% by weight.

Crushed particles (D):

particles obtained by crushing a resin composition (ii) obtained by polymerizing a composition comprising

methyl methacrylate or a monomer mixture of methyl methacrylate as the main component with other vinyl monomer having one vinyl group in the molecule or its partial polymer syrup (1) in an amount of 20 to 50% by weight based on the composition (ii),

a cross-linkable vinyl monomer (2) having two or more vinyl

groups in the molecule in an amount of 0.01 to 10% by weight based on (1),

and at least one inorganic filler (3) selected from aluminum hydroxide, magnesium hydroxide, calcium carbonate and silica, and

crushed particles (4) having an average particle size of 0.24 to 0.65 mm and containing substantially no particles having a particle size of less than 0.1 mm and particles having a particle size of over 0.8 mm, obtained by crushing a resin composition (i) obtained by polymerization-hardening a composition containing methyl methacrylate or a monomer mixture of methyl methacrylate as the main component with other vinyl monomer having one vinyl group in the molecule or its partial polymer syrup (a) in an amount of 20 to 50% by weight in the composition (ii), a cross-linkable vinyl monomer (b) having two or more vinyl groups in the molecule in an amount of 0.01 to 10% by weight based on (a), at least one inorganic filler (c) selected from aluminum hydroxide, magnesium hydroxide, calcium carbonate and silica, and inorganic fillers for coloration (d) other than the inorganic fillers (c) in an amount of 0.05 to 5% by weight in the composition (i), in an amount of 5 to 30% by weight based on the composition (ii).

2. The stone-like artificial marble according to Claim 1, wherein the inorganic fillers for coloration other than the inorganic fillers (C) are contained in an amount of 0.05 to 5% by weight in the resin composition (ii) in the component (D).

3. The stone-like artificial marble according to Claim 1,

wherein the inorganic fillers for coloration other than the inorganic fillers (C) are further contained in an amount of 0.05 to 5% by weight, in addition to the components (A), (B), (C) and (D) constituting the stone-like artificial marble.

(Detailed Description of the Invention)

(0001)

(Field of the Invention)

The present invention relates to stone-like artificial marble.

(0002)

(Prior Art)

Artificial marble is recently used in a lot of applications such as washing and dressing tables, bath tubs, tables, wall materials, floor materials, furniture, interior small goods, seal impressions and the like in addition to kitchen top boards since the artificial marble has excellent texture, excellent strength and excellent weather resistance not inferior in those of natural marble and additionally, easily executed and processed as compared with natural marble.

(0003)

As raw materials of artificial marble having features that it is light in weight and is non-porous, there are conventionally known melamine decorative boards, gel-coated artificial marble, acrylic artificial marble, polyester-based artificial marble and the like. Of them, melamine decorative plates and gel-coated artificial marble manifest difficulties in partial repairing and post processing due to patterning work only on

the surface, further, have small strength. Acrylic artificial marble and polyester-based artificial marble have texture and strength specific to solid materials, and particularly, acrylic artificial marble has a lot of merits that it is excellent also in processability and weather resistance.

(0004)

Regarding stone-like artificial marble, JP-B No. 61-24357 described, for example, those manifesting stone-like tone obtained by dispersing quartz, glass, marble, crushed stones such as mica and the like, or resin ground materials such as ABS resins, epoxy resins, melamine resins, phenol resins and the like. The particle size of a resin ground material dispersed for manifestation of stone-like tone on artificial marble is mainly from about 100 to 800 μm , and recently, for obtaining appearance nearer to natural stone, those containing dispersed particles of large particle size of about 100 to 5000 μm are widely spread.

(0005)

However, stone-like artificial marble has demerits that it is slightly inferior in strength, impact resistance and crack resistance to conventional artificial marble of single pattern having no particle patterns, since dispersed particles for manifestation of stone-like tone are present inside. Further, this decrease in physical properties manifests tends to become remarkable with increase in the particle size of dispersed particles.

(0006)

Therefore, stone-like artificial marble containing dispersed particles of large particle size has a problem that it is further inferior in physical properties as compared with conventional artificial marble containing dispersed particles of smaller particle size. Because of this reason, there is a problem that a crack defect tends to occur with decrease in heat crack resistance when used under an environment of significant temperature change such as, for example, in kitchen top boards and the like.

(0007)

(Problems to be solved by the Invention)

As one reason for decrease in physical properties due to present of dispersed particles in stone-like artificial marble, a deficiency of interface adhesion between stone-like particles and peripheral portions is envisaged. On the other hand, it is also hypothesized that because of a large difference in substance constitution between stone-like particles and peripheral portions, resultantly in physical properties, a specificity occurs and a tendency of strain on the peripheral regions is made, inducing decrease in physical properties. Then, an object of the present invention is to provide stone-like artificial marble excellent in heat crack resistance by allowing particles imparting stone-like tone to contain particles of the same composition as this, for relaxing the latter factor.

(0008)

(Means for solving the Problems)

The above-mentioned object is solved by the present

invention. The gist of the present invention is as described below. Namely, the present invention provides stone-like artificial marble obtained by polymerization-hardening a composition comprising methyl methacrylate or a monomer mixture of methyl methacrylate as the main component with other vinyl monomer having one vinyl group in the molecule or its partial polymer syrup (A) in an amount of 20 to 50% by weight based on the whole composition, a cross-linkable vinyl monomer having two or more vinyl groups in the molecule (B) in an amount of 0.01 to 10% by weight based on (A), and at least one inorganic filler (C) selected from aluminum hydroxide, magnesium hydroxide, calcium carbonate and silica and crushed particles (D) having an average particle size of 0.24 to 2.8 mm and containing substantially no particles having a particle size of less than 0.1 mm and particles having a particle size of over 5 mm, in an amount of 5 to 25% by weight based on the whole composition, wherein the total amount of inorganic fillers in the component (C) and the component (D) is 30 to 70% by weight. Crushed particles (D):

particles obtained by crushing a resin composition (ii) obtained by polymerizing a composition comprising

methyl methacrylate or a monomer mixture of methyl methacrylate as the main component with other vinyl monomer having one vinyl group in the molecule or its partial polymer syrup (1) in an amount of 20 to 50% by weight based on the composition (ii),

a cross-linkable vinyl monomer (2) having two or more vinyl

groups in the molecule in an amount of 0.01 to 10% by weight based on (1),

at least one inorganic filler (3) selected from aluminum hydroxide, magnesium hydroxide, calcium carbonate and silica, and

crushed particles (4) having an average particle size of 0.24 to 0.65 mm and containing substantially no particles having a particle size of less than 0.1 mm and particles having a particle size of over 0.8 mm, obtained by crushing a resin composition (i) obtained by polymerization-hardening a composition containing methyl methacrylate or a monomer mixture of methyl methacrylate as the main component with other vinyl monomer having one vinyl group in the molecule or its partial polymer syrup (a) in an amount of 20 to 50% by weight in the composition (ii), a cross-linkable vinyl monomer (b) having two or more vinyl groups in the molecule in an amount of 0.01 to 10% by weight based on (a), at least one inorganic filler (c) selected from aluminum hydroxide, magnesium hydroxide, calcium carbonate and silica, and inorganic fillers for coloration (d) other than the inorganic fillers (c) in an amount of 0.05 to 5% by weight in the composition (i), in an amount of 5 to 30% by weight based on the composition (ii).

(0009)

The present invention is constituted of a composition containing a copolymer obtained by copolymerizing a cross-linkable vinyl monomer having two or more vinyl groups in the molecule to an acrylic resin composition having methyl

methacrylate as the main constituent unit, and an inorganic fillers and resin particles uniformly dispersed in this copolymer.

(0010)

As the acrylic resin component constituting the main body of the stone-like artificial marble of the present invention, methyl methacrylate or a monomer mixture of methyl methacrylate as the main component with other vinyl monomer having one vinyl group in the molecule or its partial polymer syrup (A) is used. Specific examples thereof include methyl methacrylate, or monomer mixtures of 80% by weight or more of methyl methacrylate and 20% by weight or less of one or more vinyl monomers having one vinyl group in the molecule copolymerizable with methyl methacrylate, for example, α , β -ethylenically unsaturated compounds such as vinyl acetate, styrene, methyl acrylate, ethyl acrylate, butyl acrylate, cyclohexyl acrylate, ethyl methacrylate, butyl methacrylate, cyclohexane methacrylate and the like, and partially polymer syrups thereof. The use ratio of these monomers or monomer mixtures or partial polymer syrups constituting the acrylic resin composition is from 20 to 50% by weight based on the whole composition.

(0011)

Of them, syrups which are partial polymers of the above-mentioned monomers or monomer mixtures are preferably used. For obtaining the partial polymer syrup, there are known a method in which a methyl methacrylate homopolymer or a mixture containing this as the main component and a vinyl monomer is

polymerized and the polymerization is stopped on the way, a method in which a polymer containing methyl methacrylate as the main constituent unit previously polymerized by block polymerization or suspension polymerization is dissolved in a methyl methacrylate monomer, and any of them can be used.

(0012)

Merits of use of the partial polymer syrup in the present invention include: (1) In adding inorganic fillers and particles to a polymerizable raw material, deposition of these additives can be prevented by controlling the viscosity of a polymerizable raw material, syrup. (2) In polymerizing a polymerizable raw material, hardening time can be shortened, to improve productivity, and the like.

(0013)

The cross-linkable vinyl monomer (B) having two or more vinyl groups in the molecule is compounded in a proportion of 0.01 to 10% by weight, preferably 0.5 to 4% by weight based on (A). As the cross-linkable vinyl monomer (B), (meth)acrylates compounds such as ethylene glycol dimethacrylate, trimethylolpropane trimethacrylate and the like are listed.

(0014)

The inorganic filler (C) used in the present invention is at least one selected from aluminum hydroxide, calcium carbonate, magnesium hydroxide and silica, and preferable is aluminum hydroxide. This inorganic filler preferably has a particle size of 1 to 150 μm and an average particle size of 10 to 100 μm . If the particle size is much smaller than this range, light

permeability of a molded article lowers, and if the particle size is too large, a decrease in physical properties of a molded article is caused.

(0015)

When the inorganic filler (C) is added in excess, decrease in strength is caused, and when added in too small amount, texture of the resulting artificial marble is lost. By this reason, the addition amount of the inorganic filler (C) is preferably 30 to 70% by weight, more preferably 35 to 65% by weight when the total amount is 100% by weight. The use ratio of this inorganic filler is an amount as sum of inorganic fillers contained in the crushed particles (D) used in obtaining the stone-like artificial marble of the present invention.

(0016)

Those obtained by treating the surface of this inorganic filler with, for example, a silane-based coupling material, titanate-based coupling material, stearic acid and the like can be used likewise.

(0017)

The present invention is obtained by polymerization-hardening a composition containing crushed particles (D) having an average particle size of 0.24 to 2.8 mm and containing substantially no particles having a particle size of less than 0.1 mm and particles having a particle size of over 5 mm, in an amount of 5 to 25% by weight based on the whole composition and in which the total amount of inorganic fillers in the component (C) and the component (D) is 30 to 70% by weight.

(0018)

Then, the above-mentioned crushed particles (D) will be described. The crushed particles (D) are particles obtained by crushing a resin composition obtained by polymerization-hardening a composition comprising methyl methacrylate or a monomer mixture of methyl methacrylate as the main component with other vinyl monomer having one vinyl group in the molecule or its partial polymer syrup (1) in an amount of 20 to 50% by weight based on the composition (ii), a cross-linkable vinyl monomer (2) having two or more vinyl groups in the molecule in an amount of 0.01 to 10% by weight based on (1), at least one inorganic filler (3) selected from aluminum hydroxide, magnesium hydroxide, calcium carbonate and silica, and crushed particles (4) having an average particle size of 0.24 to 0.65 mm and containing substantially no particles having a particle size of less than 0.1 mm and particles having a particle size of over 0.8 mm, obtained by crushing a resin composition (i) obtained by polymerization-hardening a composition containing methyl methacrylate or a monomer mixture of methyl methacrylate as the main component with other vinyl monomer having one vinyl group in the molecule or its partial polymer syrup (a) in an amount of 20 to 50% by weight in the composition (ii), a cross-linkable vinyl monomer (b) having two or more vinyl groups in the molecule in an amount of 0.01 to 10% by weight based on (a), at least one inorganic filler (c) selected from aluminum hydroxide, magnesium hydroxide, calcium carbonate and silica, and inorganic fillers for coloration (d) other than the inorganic

fillers (c) in an amount of 0.05 to 5% by weight in the composition (i), added in an amount of 5 to 30% by weight based on the composition (ii).

(0019)

The components (1), (2) and (3) constituting the resin composition (ii) used in producing the crushed particles (D) and the components (a), (b) and (c) constituting the composition (i) are the same as the above-mentioned components A, B and C used in the present invention. In producing the composition (i) in the crushed particles (D), an inorganic filler for coloration (d) other than the component (c) corresponding to the component (C) in the present invention is used. The use amount of the inorganic filler for coloration (d) is 0.05 to 5% by weight in the composition (i). The inorganic filler for coloration may be added into the composition (ii), or both of the compositions (i) and (ii). It is compounded in the crushed particles (D) by addition to the component (i) and/or the component (ii). The amount is preferably from 0.05 to 5% by weight in the crushed particles (D).

(0020)

If the particle size of particles obtained by crushing the resin composition (i) which is an intermediate raw material of particle obtained by crushing the resin composition (ii) is too large, heat crack resistance is not improved, and when too small, the viscosity of a raw material in the form of slurry compounded in a process of producing the resin composition (ii) increases to make polymerization-hardening difficult, therefore, the

particle size is preferably from 100 to 800 μm .

(0021)

When the addition amount of particles obtained by crushing the resin composition (i) in a process of obtaining the resin composition (ii) is too large, the viscosity of a raw material in the form of slurry compounded in a process of producing the resin composition (ii) increases to make polymerization-hardening difficult, and when too small, heat crack resistance is not improved, therefore, the addition amount is preferably from 5 to 30% by weight, more preferably from 10 to 25% by weight when the total amount of the resin composition (ii) is 100% by weight.

(0022)

When the particle size of the crushed particles (D) imparting stone-like tone to the stone-like artificial marble of the present invention is too small, the viscosity of a raw material in the form of slurry compounded in a process of producing the stone-like artificial marble increases to make polymerization-hardening difficult. When too large, heat crack resistance decreases. Therefore, the particle size is preferably from 100 to 5000 μm , more preferably from 700 to 2800 μm .

(0023)

When the addition amount of the crushed particles (D) imparting stone-like tone is too large, heat crack resistance decreases, and when too small, natural stone-like appearance is not obtained, therefore, the addition amount is preferably

from 5 to 25% by weight, more preferably from 10 to 20% by weight when the total amount of the stone-like artificial marble is 100% by weight. To the stone-like artificial marble, crushed particles of the resin composition (i) may be directly added, in addition to the crushed particles of the resin composition (D).

(0024)

In the stone-like artificial marble, marble containing particles imparting stone-like tone does not obtain clear stone-like appearance having high commercial value until cutting of its surface. For this, it is preferable to cut the surface to a depth at least corresponding to 1/2 of the thickness of the maximum particle size of the crushed particles (D).

(0025)

To crushed particles (D) imparting the stone-like artificial marble of the present invention and stone-like tone, various additives, for example, ultraviolet absorbers, flame retardants, antimicrobial agents, releasing agents, fluidizing agents and thickening agents can be added.

(0026)

As resin composition composed of the above-mentioned methyl methacrylate or a monomer mixture of methyl methacrylate as the main component or its partial polymer syrup (A), cross-linkable vinyl monomer (B), inorganic filler (C) and crushed particles (D) is subsequently polymerization-hardened.

(0027)

In the method of polymerization-hardening the resin

composition, an appropriate polymerization initiator is added to the resin composition, and flown in the form of slurry into a mold frame and heat-polymerized. As the polymerization means, there are mentioned redox polymerization, a method of adding a heat reactive polymerization initiator and heat-polymerizing the mixture, and the like. Of them, redox polymerization is excellent as an industrially applicable method from the standpoint of simplicity of the process, and the like.

(0028)

Redox polymerization of a polymer having a methyl methacrylate as the main constituent unit is conducted in combination of an acyl peroxide such as benzoyl peroxide and the like with an amine compound such as N,N-dimethylaniline, N,N-diethylaniline, N,N-dimethylparaydine and the like, or in combination of a peroxy compound such as tertiary butyl peroxy maleic acid and the like with a mercaptane compound such as glycol dimercapto acetate and the like. Actually, an oxidizer is previously mixed and dispersed in a raw material in the form of slurry, and after sufficient mixing of raw materials, a reducing and if necessary, auxiliaries such as calcium hydroxide and water and the like are added and the mixture is further stirred. By this, polymerization is promoted depending o the amount of a chemical added, and further in this process, heating or heat insulation is effected, if necessary, to obtain a hardened substance.

(0029)

The procedure of polymerization-hardening the resin

composition (i) and the resin composition (ii) for obtaining the crushed particles (D) in the present invention is conducted in the same manner as in the above-mentioned polymerization-hardening of the resin composition.

(0030)

As the inorganic fillers for coloration (d) other than the inorganic fillers (c) selected from aluminum hydroxide, magnesium hydroxide, calcium carbonate and silica, added to the resin composition (i) in obtaining the crushed particles (D), there are used inorganic pigments such as titanium white, zinc oxide, lead white, carbon black, vermilion, cadmium red, yellow lead, ultramarine, cobalt blue, cobalt violet and the like. The use amount of these inorganic fillers for coloration is from 0.05 to 5% by weight in the composition. As the coloring materials in the present invention, organic pigments such as azo, triphenylmethane, quinoline, anthraquinoline and phthalocyanine-based pigments and the like can be used together.

(0031)

Regarding inorganic fillers in the stone-like artificial marble of the present invention, the total amount of inorganic fillers contained in the crushed particles (D) added in addition to the components (C) added is from 30 to 70%.

(0032)

Cross-linking by addition of the cross-linkable copolymer compound (B) of the resin composition constituting a continuous layer of the stone-like artificial marble in the present invention shows an effect of improving the strength and pollution

resistance of the stone-like artificial marble. However, excess addition thereof deteriorates processability of the resulted stone-like artificial marble. Addition of the cross-linkable copolymer compositions (2) and (b) in obtaining the crushed particles (D) improves crushing property of a polymerized hardened substance by its cross-linking effect, and suppresses increase in the viscosity of a raw material in the form of slurry before polymerization hardening by addition of the crushed particles.

(0033)

(Examples)

Next, the present invention will be described by the following examples and comparative examples. In the descriptions, "%" means % by weight. The bending rupture test used for evaluation was measured according to JIS-6911.

(0034)

The heat crack resistance test was conducted by the following method. An artificial marble sheet is cut into a 400 mm square, and the center part of the sheet is cut into 100 mm square using a high speed router. R of the corner in this case is 10 mm. This cut part is irradiated with an infrared lamp from the upper direction, and the temperature of the sheet is raised up to 90°C over 30 minutes. This temperature is maintained for 30 minutes, then, the lamp is put out and the sheet is left to be cooled for 120 minutes down to room temperature. Thereafter, the infrared lamp is lit, and the temperature of the sheet is raised up to 90°C. In a process of repeating this temperature cycle,

the number of the temperature cycle before generation of crack is used as an index for heat crack resistance. Usually, a durability of 20 cycles or more is observed, it stands actual use.

(0035)

[Example 1]

3658 g of a methyl methacrylate syrup composed of 20% of polymethyl methacrylate and 80% of methyl methacrylate, 6200 g of an aluminum hydroxide powder (manufactured by Nippon Light Metal Co., Ltd., trade name: "BS-33", also in the followings), 80 g of tertiary butyl peroxy maleic acid (manufactured by NOF Corp., trade name: "Perbutyl MA", also in the followings), 42 g of ethylene glycol dimethacrylate (manufactured by Mitsubishi Rayon Co., Ltd., trade name: "Acryester ED", also in the followings), and 50 g of a black paste as a coloring agent were mixed, and stirred by a mixer.

(0036)

After de-foaming of the resulted mixed slurry in a vacuum vessel, 12 g of glycol dimer capto acetate (manufactured by Yodo Kagaku K.K., "GDMA", also in the followings) and 8 g of de-ionized water were further added and the mixture was stirred. This slurry was poured into a mold frame of about 60 cm square on which a polyvinyl alcohol film (hereinafter, PVA film) had been laid, and on this, a PVA film was pasted. This was left in a urethane heat insulation box for 30 minutes, to obtain a hardened substance in the form of sheet. Then, this hardened substance was coarsely crashed by a hammer, further,

finely-crashed by a stamp mill. This crashed substance was classified on a sieve to obtain particles (A1) having a particle size of 104 to 701 μm and an average particle size of 340 μm .
(0037)

3658 g of a methyl methacrylate syrup composed of 20% of polymethyl methacrylate and 80% of methyl methacrylate, 5200 g of an aluminum hydroxide powder, 80 g of tertiary butyl peroxy maleic acid, 42 g of ethylene glycol dimethacrylate, 50 g of a white paste as a coloring agent and 1000 g (10% by weight) of the particles (A1) were mixed and stirred in a mixer.
(0038)

This mixed slurry was de-foamed in a vacuum vessel, then, 12 g of glycol dimer capto acetate and 8 g of de-ionized water were further added and the mixture was stirred. This slurry was poured into a mold frame of about 60 cm square on which a polyvinyl alcohol film had been laid, and on this, a PVA film was pasted. This was left in a urethane heat insulation box for 30 minutes, to obtain a hardened substance in the form of sheet on which the particles (A1) had been uniformly dispersed on the whole surface. Then, this hardened substance was coarsely crashed by a hammer, further, finely-crashed by a stamp mill. This crashed substance was classified on a sieve to obtain particles (B1) having a particle size of 104 to 4699 μm and an average particle size of 1790 μm .

(0039)

3658 g of a methyl methacrylate syrup composed of 20% of polymethyl methacrylate and 80% of methyl methacrylate, 4700

g of an aluminum hydroxide powder, 80 g of tertiary butyl peroxy maleic acid, 42 g of ethylene glycol dimethacrylate, and 1500 g (15% by weight) of the particles (B1) were mixed and stirred in a mixer.

(0040)

This mixed slurry was de-foamed in a vacuum vessel, then, 12 g of glycol dimer capto acetate and 8 g of de-ionized water were further added and the mixture was stirred. This slurry was poured into a mold frame of about 60 cm square on which a PVA film had been laid, and on this, a PVA film was pasted. This was left in a urethane heat insulation box for 30 minutes, to obtain a hardened substance in the form of sheet on which the particles (B1) had been uniformly dispersed on the whole surface.

(0041)

The surface of this hardened substance was cut at a thickness of 2 mm from the surface by a carpenter planar, then, polished with sand papers of No. 120, No. 400 and No. 600 in this order, to obtain natural stone-like clear stone-like artificial marble having high commercial value of 600×600×13 mm.

(0042)

Tips for bending test were cut out from this artificial marble, and the bending rupture test was performed. As a result, the elongation at rupture was 1.04%, the rupture strength was 591 kgf/cm², and the modulus of elasticity was 6.7×10^4 kgf/cm². Using the same sheet, the heat crack test was performed. As a result of the heat crack resistance test, this sheet did not cause cracking even after completion of 20 cycles.

(0043)

[Example 2]

Particles (A1) were obtained in the same manner as in Example 1. Then, a hardened substance in the form of sheet on which the particles (A1) had been uniformly dispersed on the whole surface was obtained in the same manner as in the procedure of obtaining the particles (B1) in Example 1 except that the use amount of the aluminum hydroxide powder was 4400 g and the use amount of the particles (A1) was 1800 g (18%). This hardened substance was coarsely crashed by a hammer, further, finely-crashed by a stamp mill, then, classified on a sieve to obtain particles (B2) having a particle size of 104 to 4699 μm and an average particle size of 1790 μm .

(0044)

A hardened substance in the form of sheet on which the particles (B2) had been uniformly dispersed on the whole surface was obtained in the same manner as in Example 1 except that 1500 g (15%) of the particles (B1) were substituted by 1500 g (15%) of the particles (B2).

(0045)

The resulted hardened substance was treated in the same manner as in Example 1 to obtain natural stone-like clear stone-like artificial marble having high commercial value of 600 mm \times 600 mm \times 13 mm. This artificial marble had an elongation at rupture of 1.05%, a rupture strength of 596 kgf/cm², and a modulus of elasticity of 6.7 \times 10⁴ kgf/cm². As a result of the heat crack resistance test, this sheet did not cause cracking even

after completion of 20 cycles.

(0046)

[Example 3]

Particles (A1) were obtained in the same manner as in Example 1. Then, a hardened substance in the form of sheet on which the particles (A1) had been uniformly dispersed on the whole surface was obtained in the same manner as in the procedure of obtaining the particles (B1) in Example 1 except that the use amount of the aluminum hydroxide powder was 3700 g and the use amount of the particles (A1) was 2500 g (25%). This hardened substance was coarsely crashed by a hammer, further, finely-crashed by a stamp mill, then, classified on a sieve to obtain particles (B3) having a particle size of 104 to 4699 μm and an average particle size of 1790 μm .

(0047)

A hardened substance in the form of sheet on which the particles (B3) had been uniformly dispersed on the whole surface was obtained in the same manner as in Example 1 except that 1500 g (15%) of the particles (B1) were substituted by 1500 g (15%) of the particles (B3).

(0048)

The resulted hardened substance was treated in the same manner as in Example 1 to obtain natural stone-like clear stone-like artificial marble having high commercial value of 600 mm \times 600 mm \times 13 mm. This artificial marble had an elongation at rupture of 1.11%, a rupture strength of 602 kgf/cm², and a modulus of elasticity of 6.5×10^4 kgf/cm². As a result of the heat

crack resistance test, this sheet did not cause cracking even after completion of 20 cycles.

(0049)

[Comparative Example 1]

3658 g of a methyl methacrylate syrup composed of 20% of polymethyl methacrylate and 80% of methyl methacrylate, 6200 g of an aluminum hydroxide powder, 80 g of tertiary butyl peroxy maleic acid, 42 g of ethylene glycol dimethacrylate and 50 g of a white paste as a coloring agent were mixed, and stirred by a mixer.

(0050)

This mixed slurry was de-foamed in a vacuum vessel, then, 12 g of glycol dimer capto acetate and 8 g of de-ionized water were further added and the mixture was stirred. This slurry was poured into a mold frame of about 60 cm square on which a PVA had been laid, and on this, a PVA film was pasted. This was processed in the same manner as in Example 1 to obtain a hardened substance in the form of sheet. This hardened substance was coarsely crashed by a hammer, further, finely-crashed by a stamp mill, and this crashed substance was classified on a sieve to obtain particles (B4) having a particle size of 104 to 4699 μm and an average particle size of 1790 μm .

(0051)

3658 g of a methyl methacrylate syrup composed of 20% of polymethyl methacrylate and 80% of methyl methacrylate, 4700 g of an aluminum hydroxide powder, 80 g of tertiary butyl peroxy maleic acid, 42 g of ethylene glycol dimethacrylate, and

1500 g (15% by weight) of the particles (B4) were mixed and stirred in a mixer. This mixed slurry was de-foamed in a vacuum vessel, then, 12 g of glycol dimercapto acetate and 8 g of de-ionized water were further added and the mixture was stirred. This slurry was poured into a mold frame of about 60 cm square on which a PVA film had been laid, and on this, a PVA film was pasted. This was processed in the same manner as in Example 1, to obtain a hardened substance in the form of sheet on which the particles (B4) had been uniformly dispersed on the whole surface.

(0052)

The resulted hardened substance was treated in the same manner as in Example 1 to obtain natural stone-like clear stone-like artificial marble of 600 mm×600 mm×13 mm. This artificial marble had an elongation at rupture of 0.97%, a rupture strength of 570 kgf/cm², and a modulus of elasticity of 6.9×10⁴ kgf/cm². As a result of the heat crack resistance test, this sheet showed cracking after 10 cycles.

(0053)

[Comparative Example 2]

Particles (A1) were obtained in the same manner as in Example 1. Then, a hardened substance in the form of sheet on which the particles (A1) had been uniformly dispersed on the whole surface was obtained in the same manner as in the procedure of obtaining the particles (B1) in Example 1 except that the use amount of the aluminum hydroxide powder was 5900 g and the use amount of the particles (A1) was 300 g (3%). This hardened substance was

coarsely crashed by a hammer, further, finely-crashed by a stamp mill, then, classified on a sieve to obtain particles (B5) having a particle size of 104 to 4699 μm and an average particle size of 1790 μm .

(0054)

A hardened substance in the form of sheet on which the particles (B5) had been uniformly dispersed on the whole surface was obtained in the same manner as in Example 1 except that 1500 g (15%) of the particles (B1) were substituted by 1500 g (15%) of the particles (B5).

(0055)

The resulted hardened substance was treated in the same manner as in Example 1 to obtain natural stone-like clear stone-like artificial marble of 600 mm \times 600 mm \times 13 mm. This artificial marble had an elongation at rupture of 0.95%, a rupture strength of 576 kgf/cm², and a modulus of elasticity of 6.8×10^4 kgf/cm². As a result of the heat crack resistance test, this sheet showed cracking after 10 cycles.

(0056)

[Comparative Example 3]

Particles (A1) were obtained in the same manner as in Example 1. 3658 g of a methyl methacrylate syrup composed of 20% of polymethyl methacrylate and 80% of methyl methacrylate, 2700 g of an aluminum hydroxide powder, 80 g of tertiary butyl peroxy maleic acid, 42 g of ethylene glycol dimethacrylate, 50 g of a white paste as a coloring agent and 3500 g (35% by weight) of the particles (A1) were mixed, and stirred by a mixer. However,

during stirring, the viscosity of this raw material in the form of slurry increased, stirring became difficult, and flowability was lost and pouring into a mold frame was impossible.

(0057)

[Comparative Example 4]

Particles (A3) were obtained in the same manner as in Example 3. 3658 g of a methyl methacrylate syrup composed of 20% of polymethyl methacrylate and 80% of methyl methacrylate, 5900 g of an aluminum hydroxide powder, 80 g of tertiary butyl peroxy maleic acid, 42 g of ethylene glycol dimethacrylate, 300 g (3% by weight) of the particles (B3) were mixed, and stirred by a mixer.

(0058)

This mixed slurry was de-foamed in a vacuum vessel, then, 12 g of glycol dimercapto acetate and 8 g of de-ionized water were further added and the mixture was stirred. This slurry was poured into a mold frame of about 60 cm square on which a PVA film had been laid, and on this, a PVA film was pasted. This was processed in the same manner as in Example 1, to obtain a hardened substance in the form of sheet on which the particles (B3) had been uniformly dispersed on the whole surface.

(0059)

The resulted hardened substance was subjected to surface cutting and polishing in the same manner as in Example 1, however, its appearance was far from that of natural stone since the number particles emerging on the surface was small.

(0060)

[Comparative Example 5]

Particles (A3) were obtained in the same manner as in Example 3. Then, a hardened substance in the form of sheet on which the particles (B3) had been uniformly dispersed on the whole surface was obtained in the same manner except that the use amount of the aluminum hydroxide powder was changed from 5900 g to 3200 g and the use amount of the particles (B3) was changed from 300 g (3%) to 3000 g (30%).

(0061)

This hardened substance was treated in the same manner as in Example 1 to obtain natural stone-like clear stone-like artificial marble of 600 mm×600 mm×13 mm. This artificial marble had an elongation at rupture of 0.95%, a rupture strength of 569 kgf/cm², and a modulus of elasticity of 6.5×10^4 kgf/cm². As a result of the heat crack resistance test, this sheet showed cracking after 9 cycles.

(0062)

[Comparative Example 6]

Particles (A2) having a particle size of 833 to 4699 μm and an average particle size of 2520 μm were obtained in the same manner as in Example 1. Then, a hardened substance in the form of sheet on which the particles (A2) had been uniformly dispersed on the whole surface was obtained in the same manner as in the procedure of obtaining the particles (B1) in Example 1 except that the use amount of the aluminum hydroxide powder was 3700 g and the use amount of the particles (A2) was 2500 g (25%). This hardened substance was coarsely crashed by a hammer, further,

finely-crashed by a stamp mill, then, classified on a sieve to obtain particles (B7) having a particle size of 104 to 4699 μm and an average particle size of 1790 μm .

(0063)

A hardened substance in the form of sheet on which the particles (B7) had been uniformly dispersed on the whole surface was obtained in the same manner as in Example 1 except that 1500 g (15%) of the particles (B1) were substituted by 1500 g (15%) of the particles (B7).

(0064)

The resulted hardened substance was treated in the same manner as in Example 1 to obtain natural stone-like clear stone-like artificial marble of 600 mm \times 600 mm \times 13 mm. This artificial marble had an elongation at rupture of 0.99%, a rupture strength of 580 kgf/cm², and a modulus of elasticity of 6.5×10^4 kgf/cm². As a result of the heat crack resistance test, this sheet showed cracking after 16 cycles.

(0065)

[Comparative Example 7]

Particles (A3) having a particle size of 53 to 88 μm and an average particle size of 70 μm were obtained in the same manner as in Example 1. 3658 g of a methyl methacrylate syrup composed of 20% of polymethyl methacrylate and 80% of methyl methacrylate, 3700 g of an aluminum hydroxide powder, 80 g of tertiary butyl peroxy maleic acid, 42 g of ethylene glycol dimethacrylate, 50 g of a white paste as a coloring agent and 2500 g (25% by weight) of the particles (A3) were mixed, and stirred by a mixer. However,

during stirring, the viscosity of this raw material in the form of slurry increased, stirring became difficult, and flowability was lost and pouring into a mold frame was impossible.

(0066)

[Comparative Example 8]

Particles (A1) were obtained in the same manner as in Example 1. Then, a hardened substance in the form of sheet on which the particles (A1) had been uniformly dispersed on the whole surface was obtained in the same manner as in the procedure of obtaining the particles (B1) in Example 1 except that the use amount of the aluminum hydroxide powder was 3700 g and the use amount of the particles (A1) was 2500 g (25%). This hardened substance was coarsely crashed by a hammer, further, finely-crashed by a stamp mill, then, classified on a sieve to obtain particles (B9) having a particle size of 5613 to 10000 μm and an average particle size of 6810 μm .

(0067)

A hardened substance in the form of sheet on which the particles (B9) had been uniformly dispersed on the whole surface was obtained in the same manner as in Example 1 except that 1500 g (15%) of the particles (B1) were substituted by 1500 g (15%) of the particles (B9).

(0068)

The resulted hardened substance was treated in the same manner as in Example 1 to obtain natural stone-like clear stone-like artificial marble of 600 mm \times 600 mm \times 13 mm. This artificial marble had an elongation at rupture of 0.88%, a

rupture strength of 539 kgf/cm², and a modulus of elasticity of 6.5×10⁴ kgf/cm². As a result of the heat crack resistance test, this sheet showed cracking after 5 cycles.

(0069)

[Comparative Example 9]

Particles (A1) were obtained in the same manner as in Example 1. Then, a hardened substance in the form of sheet on which the particles (A1) had been uniformly dispersed on the whole surface was obtained in the same manner as in the procedure of obtaining the particles (B1) in Example 1 except that the use amount of the aluminum hydroxide powder was 3700 g and the use amount of the particles (A1) was 2500 g (25%). This hardened substance was coarsely crashed by a hammer, further, finely-crashed by a stamp mill, then, classified on a sieve to obtain particles (B10) having a particle size of 58 to 88 μm and an average particle size of 70 μm.

(0070)

3658 g of a methyl methacrylate syrup composed of 20% of polymethyl methacrylate and 80% of methyl methacrylate, 4700 g of an aluminum hydroxide powder, 80 g of tertiary butyl peroxy maleic acid, 42 g of ethylene glycol dimethacrylate, and 1500 g (15% by weight) of the particles (B20) were mixed, and stirred by a mixer. However, during stirring, the viscosity of this raw material in the form of slurry increased, stirring became difficult, and flowability was lost and pouring into a mold frame was impossible.

(0071)

[Comparative Example 10]

Particles (A4) having a particle size of 208 to 4699 μm and an average particle size of 2100 μm were obtained in the same manner as in Example 1. Then, a hardened substance in the form of sheet on which the particles (A4) had been uniformly dispersed on the whole surface was obtained in the same manner as in the procedure of obtaining the particles (B1) in Example 1 except that the use amount of the aluminum hydroxide powder was 3700 g and the use amount of the particles (A4) was 2500 g (25%). This hardened substance was coarsely crashed by a hammer, further, finely-crashed by a stamp mill, then, classified on a sieve to obtain particles (B11) having a particle size of 495 to 10000 μm and an average particle size of 3680 μm .

(0072)

A hardened substance in the form of sheet on which the particles (B11) had been uniformly dispersed on the whole surface was obtained in the same manner as in Example 1 except that 1500 g (15%) of the particles (B1) were substituted by 1500 g (15%) of the particles (B11).

(0073)

The resulted hardened substance was treated in the same manner as in Example 1 to obtain natural stone-like clear stone-like artificial marble of 600 mm \times 600 mm \times 13 mm. This artificial marble had an elongation at rupture of 0.79%, a rupture strength of 521 kgf/cm², and a modulus of elasticity of 6.5 \times 10⁴ kgf/cm². As a result of the heat crack resistance test, this sheet showed cracking after 1 cycle.

(0074)

[Comparative Example 11]

3658 g of a methyl methacrylate syrup composed of 20% of polymethyl methacrylate and 80% of methyl methacrylate, 6200 g of an aluminum hydroxide powder, 80 g of tertiary butyl peroxy maleic acid, and 50 g of a black paste as a coloring agent were mixed, and stirred by a mixer.

(0075)

This mixed slurry was de-foamed in a vacuum vessel, then, 12 g of glycol dimer capto acetate and 8 g of de-ionized water were further added and the mixture was stirred. This slurry was poured into a mold frame of about 60 cm square on which a PVA had been laid, and on this, a PVA film was pasted. This was processed in the same manner as in Example 1 to obtain a hardened substance in the form of sheet.

(0076)

This hardened substance was coarsely crashed by a hammer, further, finely-crashed by a stamp mill. In this crushing process, fine particles were not obtained easily as compared with those before hardening obtained in Example 1, and fair time was necessary for crashing into given particle size. The particles were classified on a crashing sieve to obtain particles (A5) having a particle size of 104 to 701 μm and an average particle size of 340 μm .

(0077)

3658 g of a methyl methacrylate syrup composed of 20% of polymethyl methacrylate and 80% of methyl methacrylate, 3700

g of an aluminum hydroxide powder, 80 g of tertiary butyl peroxy maleic acid, 50 g of a white paste as a coloring agent, and 2500 g (25% by weight) of the particles (A5) were mixed and stirred in a mixer. However, during stirring, the viscosity of this raw material in the form of slurry increased, stirring became difficult, and flowability was lost and pouring into a mold frame was impossible.

(0078)

[Effect of the Invention]

The stone-like artificial marble of the present invention contains particles of the same composition as that constituting stone-like artificial marble, in particles imparting stone-like tone, therefore, strain is not formed on substance constitution between stone-like particles and peripheral parts thereof, and excellent heat crack resistance not found in conventional products is obtained.

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(54) 【発明の名称】 石目調人工大理石

(57) 【要約】

【目的】 耐熱クラック性に優れた石目調人工大理石を提供する。

【構成】 メチルメタクリレート部分重合体シラップ

(A) を組成物中に20～50重量%、架橋性ビニル単量体(B)を(A)に対して0.01～10重量%、水酸化アルミニウム、水酸化マグネシウム、炭酸カルシウム及びシリカから選ばれる少なくとも1種の無機充填剤(C)、及び本発明を実施する場合と同様の組成に着色用無機充填剤を含む樹脂を粉碎した粒径0.1mm未満の粒子及び粒径5mmを超える粒子を実質的に含まず、平均粒径0.24～2.8mmである粉碎粒子(D)を全組成物中に5～25重量%含有し、(C)成分及び(D)成分中の無機充填剤の合計量が30～70重量%である組成物を重合硬化して得られた石目調人工大理石。

【特許請求の範囲】

【請求項 1】 メタクリル酸メチル又はメタクリル酸メチルを主成分とする分子内にビニル基を 1 個有する他のビニル単量体との単量体混合物若しくはその部分重合体シラップ (A) を全組成物中に 20~50 重量%、分子内に 2 個以上のビニル基を有する架橋性ビニル単量体 (B) を (A) に対して 0.01~10 重量%、水酸化アルミニウム、水酸化マグネシウム、炭酸カルシウム及びシリカから選ばれる少なくとも 1 種の無機充填剤 (C)、及び下記の粒径 0.1mm 未満の粒子及び粒径 5mm を超える粒子を実質的に含まず、平均粒径 0.24~2.8mm である粉碎粒子 (D) を全組成物中に 5~25 重量%含有し、(C) 成分及び (D) 成分中の無機充填剤の合計量が 30~70 重量%である組成物を重合硬化して得られた石目調人工大理石。

粉碎粒子 (D)

メタクリル酸メチル又はメタクリル酸メチルを主成分とする分子内にビニル基を 1 個有する他のビニル単量体との単量体混合物若しくはその部分重合体シラップ (1) を組成物 (ロ) 中に 20~50 重量%、分子内に 2 個以上のビニル基を有する架橋性ビニル単量体 (2) を

(1) に対して 0.01~10 重量%、水酸化アルミニウム、水酸化マグネシウム、炭酸カルシウム及びシリカから選ばれる少なくとも 1 種の無機充填剤 (3)、並びにメタクリル酸メチル又はメタクリル酸メチルを主成分とする分子内にビニル基を 1 個有する他のビニル単量体との単量体混合物若しくはその部分重合体シラップ

(a) を組成物 (イ) 中に 20~50 重量%、分子内に 2 個以上のビニル基を有する架橋性ビニル単量体 (b) を (a) に対して 0.01~10 重量%、水酸化アルミニウム、水酸化マグネシウム、炭酸カルシウム及びシリカから選ばれる少なくとも 1 種の無機充填剤 (c)、及び無機充填剤 (c) 以外の着色用無機充填剤 (d) を組成物 (イ) 中に 0.05~5 重量%を含有する組成物を重合硬化して得られる樹脂組成物 (イ) を粉碎した粒径 0.1mm 未満の粒子及び粒径 0.8mm を超える粒子を実質的に含まず、平均粒径 0.24~0.65mm である粉碎粒子 (4) を、組成物 (ロ) 中に 5~30 重量%を含有する組成物を重合して得られる樹脂組成物

(ロ) を粉碎した粒子。

【請求項 2】 (D) 成分における樹脂組成物 (ロ) 中に無機充填剤 (C) 以外の着色用無機充填剤が 0.05~5 重量%含有されていることを特徴とする請求項 1 の石目調人工大理石。

【請求項 3】 石目調人工大理石を構成する (A)、(B)、(C)、(D) 成分以外に更に無機充填剤 (C) 以外の着色用無機充填剤が 0.05~5 重量%含有されていることを特徴とする請求項 1 の石目調人工大理石。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は、石目調人工大理石に関する。

【0002】

【従来の技術】 人工大理石は、天然大理石に劣らない優美な質感、優れた強度、良好な耐候性を持つうに、天然大理石に比べ、施工、加工が容易であることから、近年では、キッチン天板の他、洗面化粧台、バスタブ、テーブル、壁材、床材、家具、インテリア小物、印鑑など、多くの用途に用いられてきている。

【0003】 天然大理石に比べ、軽量で、無孔質であるという特徴をもった人工大理石の素材としては、従来からメラミン化粧板、ゲルコート人工大理石、アクリル系人工大理石、ポリエステル系人工大理石などが知られている。これらの内、メラミン化粧板、ゲルコート人工大理石は、表面のみの模様出し加工のため、部分補修、後加工が難しく、さらには強度が弱いという欠点をもっている。アクリル系人工大理石、及びポリエステル系人工大理石は、ソリッド材特有の質感、強度を有し、中でもアクリル系人工大理石においては、加工性、耐候性にも優れるという多くの長所を有している。

【0004】 石目調人工大理石としては、例えば、特公昭 61-24357 号公報には、石英、ガラス、大理石、雲母などの碎石、または、ABS 樹脂、エポキシ樹脂、メラミン樹脂、フェノール樹脂などの樹脂粉碎物を分散させて、石目調を発現させたものが記載されている。これまで、人工大理石に石目調を発現させるために分散させる樹脂粉碎物の粒子径は 100~800 μ m 程度の小粒径のものが主流であったが、近年では、より天然石に近い外観を得るため、100~5000 μ m 程度の大粒径の粒子を分散させたものが広まりつつある。

【0005】 しかしながら、石目調人工大理石においては、石目調を発現させる分散粒子が内部に存在するために、従来の粒子模様のない単柄の人工大理石に比較して、強度、耐衝撃性、耐熱クラック性の面で若干劣るという欠点がある。さらに、この物性の低下は、分散粒子の粒径が大きくなるにつれ、顕著になる傾向を示す。

【0006】 したがって、大粒径の分散粒子を含む石目調人工大理石は、従来の小粒径の分散粒子を含む石目調人工大理石に比較して、さらに物性が劣るという問題がある。このことから、例えばキッチン天板など、温度変化の激しい環境で使用する場合には、耐熱クラック性の低下に伴い、クラック欠陥を発生しやすいという問題点がある。

【0007】

【発明が解決しようとする課題】 石目調人工大理石において分散粒子が存在することによる物性が低下する理由の一つとして、石目調粒子とその周辺部分との界面接着性の不足が考えられる。また、一方では、石目調粒子とその周辺部分との物質構成、延いては物性に大きな差が

あるのに起因し、特異性を生じて、その周囲に歪を起しやすくしていることが、物性低下を誘発しているとも考えられる。そこで、本発明は、後者の要因を緩和するため、石目調を与える粒子中に、さらにこれと同じ組成の粒子を含有させることにより、耐熱クラック性に優れた石目調人工大理石を提供しようとするものである。

【0008】

【課題を解決するための手段】上記課題は、本発明によって解決される。本発明の要旨とするところは次の通りである。すなわち、メタクリル酸メチル又はメタクリル酸メチルを主成分とする分子内にビニル基を1個有する他のビニル単量体との単量体混合物若しくはその部分重合体シラップ(A)を全組成物中に20~50重量%、分子内に2個以上のビニル基を有する架橋性ビニル単量体(B)を(A)に対して0.01~10重量%、水酸化アルミニウム、水酸化マグネシウム、炭酸カルシウム及びシリカから選ばれる少なくとも1種の無機充填剤(C)、及び下記の粒径0.1mm未満の粒子及び粒径5mmを超える粒子を実質的に含まず、平均粒径0.24~2.8mmである粉砕粒子(D)を全組成物中に5~25重量%含有し、(C)成分及び(D)成分中の無機充填剤の合計量が30~70重量%である組成物を重合硬化して得られる石目調人工大理石。

粉砕粒子(D)

メタクリル酸メチル又はメタクリル酸メチルを主成分とする分子内にビニル基を1個有する他のビニル単量体との単量体混合物若しくはその部分重合体シラップ(1)を組成物(ロ)中に20~50重量%、分子内に2個以上のビニル基を有する架橋性ビニル単量体(2)を

(1)に対して0.01~10重量%、水酸化アルミニウム、水酸化マグネシウム、炭酸カルシウム及びシリカから選ばれる少なくとも1種の無機充填剤(3)、並びにメタクリル酸メチル又はメタクリル酸メチルを主成分とする分子内にビニル基を1個有する他のビニル単量体との単量体混合物若しくはその部分重合体シラップ

(a)を組成物(イ)中に20~50重量%、分子内に2個以上のビニル基を有する架橋性ビニル単量体(b)を(a)に対して0.01~10重量%、水酸化アルミニウム、水酸化マグネシウム、炭酸カルシウム及びシリカから選ばれる少なくとも1種の無機充填剤(c)、及び無機充填剤(c)以外の着色用無機充填剤(d)を組成物(イ)中に0.05~5重量%を含有する組成物を重合硬化して得られる樹脂組成物(イ)を粉砕した、粒径0.1mm未満の粒子及び粒径0.8mmを超える粒子を実質的に含まず、平均粒径0.24~0.65mmである粉砕粒子(4)を、組成物(ロ)中に5~30重量%を含有する組成物を重合して得られる樹脂組成物(ロ)を粉砕した粒子。

【0009】本発明は、メタクリル酸メチルを主構成単位とするアクリル系樹脂組成物に分子内に2個以上のビ

ニル基を有する架橋性ビニル単量体を共重合させた共重合体、及び該共重合体中に均一に分散された無機充填剤並びに樹脂粒子よりなる組成物で構成されている。

【0010】本発明の石目調人工大理石の主体を構成するアクリル系樹脂成分としては、メタクリル酸メチル又はメタクリル酸メチルを主成分とする分子内にビニル基を1個有する他のビニル単量体との単量体混合物若しくはその部分重合体シラップ(A)が用いられる。具体的にはメタクリル酸メチル又はメタクリル酸メチル80重量%以上と20重量%以下のメタクリル酸メチルを共重合可能な分子内に1個のビニル基を有するビニル単量体例えば、酢酸ビニル、スチレン、メチルアクリレート、エチルアクリレート、ブチルアクリレート、シクロヘキシルアクリレート、エチルメタクリレート、ブチルメタクリレート、シクロヘキサンメタクリレート等の α 、 β -エチレン性不飽和化合物の1種または2種以上の単量体混合物若しくはこれらの部分重合体シラップである。アクリル系樹脂組成物を形成するこれら単量体又は単量体混合物もしくは部分重合体シラップの使用割合は、全組成物中20~50重量%である。

【0011】これらの中上記単量体又は単量体混合物の部分重合体であるシラップの使用が好ましい。部分重合体シラップを得るには、メタクリル酸メチル単量体又はこれを主体とするビニル単量体との混合物を重合させ途中で重合を停止させる方法、又は、塊状重合や懸濁重合によってあらかじめ重合したメタクリル酸メチルを主構成単位とする重合体を、メタクリル酸メチル単量体に溶解する方法が知られており、何れも使用できる。

【0012】本発明において部分重合体シラップを用いることの利点としては、①重合性原料に、無機充填剤と、粒子を添加する際、重合性原料であるシラップの粘度をコントロールすることによって、これら添加物の沈降を防ぐことができる。②重合性原料を重合させるに当り硬化時間を短縮でき、生産性が向上するなどが挙げられる。

【0013】分子内に2個以上のビニル基を有する架橋性ビニル単量体(B)は(A)に対して0.01~10重量%、好ましくは0.5~4重量%を配合する。架橋性ビニル単量体(B)としては、ジメタクリル酸エチレングリコール、トリメタクリル酸トリメチロールプロパン等の(メタ)アクリル酸エステル化合物が挙げられる。

【0014】本発明に用いられる無機充填剤(C)は、水酸化アルミニウム、炭酸カルシウム、水酸化マグネシウム、シリカから選ばれる少なくとも1種であるが、好ましくは水酸化アルミニウムである。この無機充填剤の粒子サイズは、粒径が1~150 μ mで、平均粒径が10~100 μ mであるものが好ましい。この範囲より粒径が小さすぎると成形物の光透過性が低下し、また、粒径が大きすぎると成形物の物性低下を招く。

【0015】無機充填剤(C)は、過剰に添加すると強度の低下を招き、反対に少なすぎると得られる人工大理石の質感が損なわれる。このことから、石目調人工大理石へは、その全量を100重量%としたとき、30~70重量%添加することが好ましく、より好ましくは35~65重量%である。この無機充填剤の使用割合は、本発明の石目調人工大理石を得る際に用いる粉碎粒子

(D)に含まれている無機充填剤の合計としての量である。

【0016】なお、この無機充填剤の表面を、例えば、シラン系カップリング材、チタネート系カップリング材、ステアリン酸等で処理したものも同様に扱うことができる。

【0017】本発明は、後記する粒径0.1mm未満の粒子及び粒径5mmを超える粒子を実質的に含まない平均粒径0.24~2.8mmである粉碎粒子(D)を全組成物中に5~25重量%含有し、且つ、(C)成分及び(D)成分中の無機充填剤の合計量が30~70重量%である組成物を重合硬化したものである。

【0018】次に上記(D)の粉碎粒子について説明する。粉碎粒子(D)は、メタクリル酸メチル又はメタクリル酸メチルを主成分とする分子内にビニル基を1個有する他のビニル単量体との単量体混合物若しくはその部分重合体シラップ(1)を組成物(ロ)中に20~50重量%、分子内に2個以上のビニル基を有する架橋性ビニル単量体(2)を上記(1)に対して0.01~10重量%、水酸化アルミニウム、水酸化マグネシウム、炭酸カルシウム及びシリカから選ばれる少なくとも1種の無機充填剤(3)と、これに、メタクリル酸メチル又はメタクリル酸メチルを主成分とする分子内にビニル基を1個有する他のビニル単量体との単量体混合物若しくはその部分重合体シラップ(a)を組成物(イ)中に20~50重量%、分子内に2個以上のビニル基を有する架橋性ビニル単量体(b)を上記(a)に対して0.01~10重量%、水酸化アルミニウム、水酸化マグネシウム、炭酸カルシウム及びシリカから選ばれる少なくとも1種の無機充填剤(c)、及び無機充填剤(c)以外の着色用無機充填剤(d)を組成物(イ)中に0.05~5重量%を含有する組成物(イ)を重合硬化し、これを粉碎して粒径0.1mm未満の粒子及び粒径0.8mmを超える粒子を実質的に含まず、平均粒径0.24~0.65mmとした粉碎粒子(4)を、組成物(ロ)に対して5~30重量%添加し、重合硬化し、次いでこれを粉碎した粒子である。

【0019】粉碎粒子(D)の製造に用いる樹脂組成物(ロ)を構成する成分(1)、(2)、(3)及び組成物(イ)を構成する成分(a)、(b)、(c)は、本発明において用いる前記A、B、Cの成分と同じである。粉碎粒子(D)における(イ)の製造においては、本発明の(C)成分に相当する(c)成分以外に着色用

無機充填剤(d)を用いる。着色用無機充填剤(d)の使用量は組成物(イ)中0.05~5重量%である。また、着色用無機充填剤は組成物(ロ)中に、又は

(イ)、(ロ)の両方に添加してもよい。この場合の使用量は(イ)又は/及び(ロ)に加えることによって

(D)中に配合される。その量は(D)中において好ましくは0.05~5重量%である。

【0020】樹脂組成物(ロ)を粉碎した粒子の中間原料である樹脂組成物(イ)を粉碎した粒子の粒径は、大きすぎると、耐熱クラック性が向上せず、また、小さすぎると樹脂組成物(ロ)を作る過程で調合されるスラリー状原料の粘度が上昇して重合硬化が困難となるため、100~800 μ mが良い。

【0021】また、樹脂組成物(ロ)を得る過程における樹脂組成物(イ)を粉碎した粒子の添加量は、多すぎると樹脂組成物(ロ)を作る過程で調合されるスラリー状原料の粘度が上昇して重合硬化が困難となるし、また、少なすぎると耐熱クラック性が向上しないことから、樹脂組成物(ロ)を全量100重量%としたとき、5~30重量%が良い。より好ましくは10~25重量%である。

【0022】本発明の石目調人工大理石に石目調を与える粉碎粒子(D)の粒径は、小さすぎると石目調人工大理石を作る過程で調合されるスラリー状原料の粘度が上昇して重合硬化が困難となるし、また、大きすぎると耐熱クラック性が低下するため100~5000 μ mが良い。より好ましくは700~2800 μ mである。

【0023】また、石目調を与える粉碎粒子(D)の添加量は、多すぎると耐熱クラック性が低下し、また少なすぎると天然石様の外観が得られないことから、石目調人工大理石を全量100重量%としたとき5~25重量%が良い。より好ましくは10~20重量%である。なお、石目調人工大理石へは、樹脂組成物(D)の粉碎粒子の他、樹脂組成物(イ)の粉碎粒子を直接添加してもよい。

【0024】石目調人工大理石において、石目調を与える粒子を含む人工大理石は、その表面を研削することにより、はじめてクリアーな商品価値の高い石目調の外観が得られる。そのためには粉碎粒子(D)の有する最大粒径の少なくとも1/2以上の厚さで表面を研削することが好ましい。

【0025】本発明の石目調人工大理石、及び石目調を与える粒子(D)には、種々の添加剤、例えば、紫外線吸収剤、難燃剤、抗菌剤、離型剤、流動化剤、増粘剤を加えることができる。

【0026】前記メタクリル酸メチル又はこれを主体とするビニル単量体混合物もしくはそれらの部分重合体シラップ(A)と架橋性ビニル単量体(B)、無機充填剤(C)及び粉碎粒子(D)からなる樹脂組成物は次いで重合硬化される。

【0027】樹脂組成物を重合硬化させる方法としては、樹脂組成物に適宜の重合開始剤を加え、スラリー状態で型枠に流し込み加熱重合する。重合手段としては、レドックス重合、又は、熱反応性重合開始剤を添加し加熱重合する方法等が挙げられる。これらのうち、設備的コストや、プロセスの簡略性などの面でレドックス重合は工業的利用方法として優れている。

【0028】メタクリル酸メチルを主構成単位とする重合体のレドックス重合は、ベンゾイルパーオキサイドなどのアシル過酸化物とN、N-ジメチルアニリン、N、N-ジエチルアニリン、N、N-ジメチルパラジジンなどのアミン化合物との組み合わせ、又はターシャリーブチルパーオキシマレイン酸などのパーオキシ化合物とグリコールジメルカプトアセテートなどのメルカプタン化合物との組み合わせなどによって行われる。実際には、まず、酸化剤を適量、スラリー状原料にあらかじめ混合分散させておき、充分に各原料が混合された後、還元剤、並びに必要に応じて水酸化カルシウム及び水等の助剤を加えてさらに混合攪拌する。そうすることにより、添加した薬剤の量に応じて重合が促進され、さらにその過程で必要に応じて加温あるいは保温することにより硬化物が得られる。

【0029】本発明において粉碎粒子(D)を得るために樹脂組成物(I)及び樹脂組成物(II)を重合硬化する手段も上記樹脂組成物の重合硬化と同様に行う。

【0030】粉碎粒子(D)を得るに当り樹脂組成物(I)に添加する水酸化アルミニウム、水酸化マグネシウム、炭酸カルシウム及びシリカから選ばれる無機充填剤(c)以外の着色用無機充填剤(d)としては、チタン白、亜鉛華、鉛白、カーボンブラック、朱、カドミウム赤、黄色鉛、群青、コバルト青、コバルト紫などの無機顔料が用いられる。これら着色用無機充填剤の使用量は、組成物中0.05~5重量%である。なお、本発明においては着色料として、アゾ系、トリフェニルメタン系、キノリン系、アントラキノン系、フタロシアニン系などの有機顔料を併用することができる。

【0031】本発明石目調人工大理石中の無機充填剤は、添加する(C)成分の外に、添加する粉碎粒子(D)に含まれる無機充填剤を合計してその量が30~70%である。

【0032】本発明において石目調人工大理石の連続層を構成する樹脂組成物の架橋性共重合化合物(B)の添加による架橋は、その石目調人工大理石の強度、及び耐汚染性を向上させる効果がある。しかし、過剰の添加は得られた石目調人工大理石の加工性を悪化させる。また、粉碎粒子(D)を得るに当り架橋性共重合化合物(2)及び(b)の添加は、その架橋効果により重合硬化物の粉碎性を向上させると共に、この粉碎粒子を添加した重合硬化前のスラリー状原料の粘度上昇を抑制する。

【0033】

【実施例】次に本発明を実施例、比較例を挙げて説明する。説明中「%」は重量%を意味する。評価に用いた曲げ破断試験はJIS-6911に準じて測定した。

【0034】また、耐熱クラック性試験は以下に示す方法で行った。人工大理石シートを400mm角に切り出し、シート中央部を高速ルーターを用いて100mm角に切り抜く。このときコーナー部分のRは10mmになるようにする。この切り抜き部分の上方より赤外線ランプを照射し、30分かけて90℃までシート温度を上げる。この温度を30分保ったのち、ランプを消し、120分間放置冷却し室温まで下げる。その後、また赤外線ランプを点灯し、90℃までシート温度を上げるという温度サイクルを繰り返していく過程で、クラックが発生するまでの温度サイクル回数をもって、耐熱クラック性能の指標とする。通常、20サイクル以上の耐久性があれば、実用に耐える。

【0035】〔実施例1〕ポリメタクリル酸メチル20%とメタクリル酸メチル80%からなるメタクリル酸メチルシラップ3658g、水酸化アルミニウム粉末(日本軽金属(株)製、商品名「BS-33」以下同)6200g、ターシャリーブチルパーオキシマレイン酸(日本油脂(株)製、商品名「パーブチルMA」以下同)80g、ジメタクリル酸エチレングリコール(三菱レイヨン(株)製、商品名「アクリエステルED」以下同)42g、着色剤として黒ペースト50gを混合し、ミキサーで攪拌した。

【0036】得られた混合スラリーを真空容器内で脱泡した後、さらに、グリコールジメルカプトアセテート(淀化学(株)製、「GDMA」以下同)12g、脱イオン水8gを添加して攪拌した。このスラリーを、ポリビニルアルコールフィルム(以下PVAフィルム)を敷いた約60cm角の型枠中に注入し、その上からPVAフィルムを張り付けた。これをウレタン保温箱中に30分放置し、シート状硬化物を得た。ついでこの硬化物をハンマーで粗粉碎し、さらにスタンプミルで微粉碎した。この粉碎物を篩いで分別して粒径104~701μm、平均粒径340μmの粒子(A1)を得た。

【0037】ポリメタクリル酸メチル20%とメタクリル酸メチル80%からなるメタクリル酸メチルシラップ3658g、水酸化アルミニウム粉末5200g、ターシャリーブチルパーオキシマレイン酸80g、ジメタクリル酸エチレングリコール42g、着色剤として白ペースト50g、粒子(A1)1000g(10重量%)を混合し、ミキサーで攪拌した。

【0038】この混合スラリーを真空容器内で脱泡した後、さらに、グリコールジメルカプトアセテート12g、脱イオン水8gを添加して攪拌した。このスラリーを、PVAフィルムを敷いた約60cm角の型枠中に注入し、その上からPVAフィルムを張り付けた。これを

ウレタン保温箱中に30分放置し、粒子(A1)が全面に均一に分散したシート状硬化物を得た。ついで、この硬化物をハンマーで粗粉碎し、さらに、スタンプミルで微粉碎した。この粉碎物を篩いで分別して粒径104~4699 μ m、平均粒径1790 μ mの粒子(B1)を得た。

【0039】ポリメタクリル酸メチル20%とメタクリル酸メチル80%からなるメタクリル酸メチルシラップ3658g、水酸化アルミニウム粉末4700g、ターシャリーブチルパーオキシマレイン酸80g、ジメタクリル酸エチレングリコール42g、粒子(B1)1500g(15重量%)を混合し、ミキサーで撹拌した。

【0040】この混合スラリーを真空容器内で脱泡した後、さらに、グリコールジメルカプトアセテート12g、脱イオン水8gを添加して撹拌した。このスラリーを、PVAフィルムを敷いた約60cm角の型枠中に注入し、その上からPVAフィルムを張り付けた。これをウレタン保温箱中に30分放置し、粒子(B1)が全面に均一に分散したシート状硬化物を得た。

【0041】この硬化物の表面を、木工用プレーナーで、表面から厚さ2mm削り、その後、120番、400番、600番のサンドペーパーで順に研磨したところ、600×600×13mmのクリアーで商品価値の高い天然石様の石目調人工大理石が得られた。

【0042】この人工大理石から、曲げ試験用チップを切り出し、曲げ破断試験を実施した。その結果、破断伸度1.04%、破断強度591kgf/cm²、弾性率6.7×10⁴kgf/cm²であった。また、同じシートを用いて耐熱クラック性試験を実施した。耐熱クラック性試験の結果このシートは20サイクル終了後も、クラックは発生しなかった。

【0043】〔実施例2〕実施例1と同様にして粒子(A1)を得た。ついで実施例1の粒子(B1)を得る処方において水酸化アルミニウム粉末の使用量を4400g、及び粒子(A1)の使用量を1800g(18%)としたほかは同様に操作して粒子(A1)が全面に均一に分散したシート状硬化物を得た。この硬化物をハンマーで粗粉碎し、さらにスタンプミルで微粉碎し、篩いで分別して104~4699 μ m、平均粒径1790 μ mの粒子(B2)を得た。

【0044】以下、実施例1において粒子(B1)1500g(15%)に変えて粒子(B2)1500(15%)としたほかは同様に操作して粒子(B2)が全面的に均一に分散したシート状硬化物を得た。

【0045】得られた硬化物を実施例1と同様に処理したところ、600mm×600mm×13mmのクリアーで商品価値の高い天然石様の石目調人工大理石が得られた。この人工大理石の破断伸度1.05%、破断強度596kgf/cm²、弾性率6.7×10⁴kgf/cm²であった。また、耐熱クラック試験の結果、20

サイクル終了後もクラックは発生しなかった。

【0046】〔実施例3〕実施例1と同様にして粒子(A1)を得た。ついで実施例1の粒子(B1)を得る処方において水酸化アルミニウム粉末の使用量を3700g、及び粒子(A1)の使用量を2500g(25%)としたほかは同様に操作して粒子(A1)が全面に均一に分散したシート状硬化物を得た。この硬化物をハンマーで粗粉碎し、さらにスタンプミルで微粉碎し、篩いで分別して粒径104~4699 μ m、平均粒径1790 μ mの粒子(B3)を得た。

【0047】以下、実施例1において粒子(B1)1500g(15%)に変えて粒子(B3)1500g(15%)としたほかは同様に操作して粒子(B3)が全面的に均一に分散したシート状硬化物を得た。

【0048】得られた硬化物を実施例1と同様に処理したところ、600mm×600mm×13mmのクリアーで商品価値の高い天然石様の石目調人工大理石が得られた。この人工大理石の破断伸度1.11%、破断強度602kgf/cm²、弾性率6.5×10⁴kgf/cm²であった。また、耐熱クラック試験の結果、20サイクル終了後もクラックは発生しなかった。

【0049】〔比較例1〕ポリメタクリル酸メチル20%とメタクリル酸メチル80%からなるメタクリル酸メチルシラップ3658g、水酸化アルミニウム粉末6200g、ターシャリーブチルパーオキシマレイン酸80g、ジメタクリル酸エチレングリコール42g、着色剤として白ペースト50gを混合し、ミキサーで撹拌した。

【0050】この混合スラリーを真空容器内で脱泡した後、さらに、グリコールジメルカプトアセテート12g、脱イオン水8gを添加して撹拌した。このスラリーを、PVAフィルムを敷いた約60cm角の型枠中に注入し、その上からPVAフィルムを張り付けた。これを実施例1と同様にしてシート状硬化物を得た。この硬化物をハンマーで粗粉碎したものを、さらにスタンプミルで微粉碎し、この粉碎物を篩いで分別して粒径104~4699 μ m、平均粒径1790 μ mの粒子(B4)を得た。

【0051】ポリメタクリル酸メチル20%とメタクリル酸メチル80%からなるメタクリル酸メチルシラップ3658g、水酸化アルミニウム粉末4700g、ターシャリーブチルパーオキシマレイン酸80g、ジメタクリル酸エチレングリコール42g、粒子(B4)1500g(15重量%)を混合し、ミキサーで撹拌した。その混合スラリーを真空容器内で脱泡した後、さらに、グリコールジメルカプトアセテート12g、脱イオン水8gを添加して撹拌した。このスラリーを、PVAフィルムを敷いた約60cm角の型枠中に注入し、その上からPVAフィルムを張り付けた。これを実施例1と同様にして粒子(B4)が全面に均一に分散したシート状硬化

物を得た。

【0052】得られた硬化物を実施例1と同様に処理したところ、600mm×600mm×13mmのクリアーで天然石様の石目調人工大理石が得られた。この人工大理石の破断伸度0.97%、破断強度570kgf/cm²、弾性率6.9×10⁴kgf/cm²であった。また、耐熱クラック試験の結果は、10サイクルでクラックが発生した。

【0053】〔比較例2〕実施例1と同様にして粒子(A1)を得た。ついで実施例1の粒子(B1)を得る処方において水酸化アルミニウム粉末の使用量を5900g、及び粒子(A1)の使用量を300g(3%)としたほかは同様に操作して粒子(A1)が全面に均一に分散したシート状硬化物を得た。この硬化物をハンマーで粗粉碎し、さらにスタンプミルで微粉碎し、篩いで分別して粒径104~4699μm、平均粒径1790μmの粒子(B5)を得た。

【0054】以下、実施例1において粒子(B1)1500g(15%)に変えて粒子(B5)1500g(15%)としたほかは同様に操作して粒子(B5)が全面的に均一に分散したシート状硬化物を得た。

【0055】得られた硬化物を実施例1と同様に処理したところ、600mm×600mm×13mmのクリアーで天然石様の石目調人工大理石が得られた。この人工大理石の破断伸度0.95%、破断強度576kgf/cm²、弾性率6.8×10⁴kgf/cm²であった。また、耐熱クラック試験の結果は、10サイクルでクラックが発生した。

【0056】〔比較例3〕実施例1と同様にして粒子(A1)を得た。ポリメタクリル酸メチル20%とメタクリル酸メチル80%からなるメタクリル酸メチルシラップ3658g、水酸化アルミニウム粉末2700g、ターシャリーブチルパーオキシマレイン酸80g、ジメタクリル酸エチレングリコール42g、着色剤として白ペースト50g、粒子(A1)3500g(35重量%)を混合し、ミキサーで攪拌した。しかしながら、攪拌途中に、このスラリー状原料の粘度が上昇し、攪拌困難となるとともに、流動性を失い、型枠への注入ができなかった。

【0057】〔比較例4〕実施例3と同様にして粒子(B3)を得た。ポリメタクリル酸メチル20%とメタクリル酸メチル80%からなるメタクリル酸メチルシラップ3658g、水酸化アルミニウム粉末5900g、ターシャリーブチルパーオキシマレイン酸80g、ジメタクリル酸エチレングリコール42gと、粒子(B3)300g(3重量%)を混合し、ミキサーで攪拌した。

【0058】この混合スラリーを真空容器中で脱泡した後、さらに、グリコールジメルカプトアセテート12g、脱イオン水8gを添加して攪拌した。このスラリーを、PVAフィルムを敷いた約60cm角の型枠中に注

入し、その上からPVAフィルムを張り付けた。これを実施例1と同様にして粒子(B3)が全面に均一に分散したシート状硬化物を得た。

【0059】得られた硬化物を実施例1と同様に表面を研削、研磨したが、表面に出現している粒子の数が少ないため、その外観は天然石とはほど遠いものであった。

【0060】〔比較例5〕実施例3と同様にして粒子(B3)を得た。ついで、比較例4において水酸化アルミニウム粉末5900gに変えて3200g、及び粒子(B3)300g(3%)に変えて粒子(B3)3000g(30%)としたほかは同様に操作して粒子(B3)が全面的に均一に分散したシート状硬化物を得た。

【0061】得られた硬化物を実施例1と同様に処理したところ、600mm×600mm×13mmのクリアーで天然石様の石目調人工大理石が得られた。この人工大理石の破断伸度0.95%、破断強度569kgf/cm²、弾性率6.5×10⁴kgf/cm²であった。また、耐熱クラック試験の結果は、9サイクルでクラックが発生した。

【0062】〔比較例6〕実施例1と同様にして、但し833~4699μm、平均粒径2520μmの粒子(A2)を得た。ついで実施例1の粒子(B1)を得る処方において水酸化アルミニウム粉末の使用量を3700g、及び粒子(A2)の使用量を2500g(25%)としたほかは同様に操作して粒子(A2)が全面に均一に分散したシート状硬化物を得た。この硬化物をハンマーで粗粉碎し、さらにスタンプミルで微粉碎し、篩いで分別して粒径104~4699μm、平均粒径1790μmの粒子(B7)を得た。

【0063】以下、実施例1において粒子(B1)1500g(15%)に変えて粒子(B7)1500g(15%)としたほかは同様に操作して粒子(B7)が全面的に均一に分散したシート状硬化物を得た。

【0064】得られた硬化物を実施例1と同様に処理したところ、600mm×600mm×13mmのクリアーで天然石様の石目調人工大理石が得られた。この人工大理石の破断伸度0.99%、破断強度580kgf/cm²、弾性率6.5×10⁴kgf/cm²であった。また、耐熱クラック試験の結果は、16サイクルでクラックが発生した。

【0065】〔比較例7〕実施例1と同様にして、但し粒径53~88μm、平均粒径70μmの粒子(A3)を得た。ポリメタクリル酸メチル20%とメタクリル酸メチル80%からなるメタクリル酸メチルシラップ3658g、水酸化アルミニウム粉末3700g、ターシャリーブチルパーオキシマレイン酸80g、ジメタクリル酸エチレングリコール42g、着色剤として白ペースト50g、粒子(A3)2500g(25重量%)を混合し、ミキサーで攪拌した。しかしながら、攪拌途中に、このスラリー状原料の粘度が上昇し、攪拌困難となると

ともに、流動性を失い、型枠への注入ができなかった。

【0066】〔比較例8〕実施例1と同様にして粒子(A1)を得た。ついで実施例1の粒子(B1)を得る処方において水酸化アルミニウム粉末の使用量を3700g、及び粒子(A1)の使用量を2500g(25%)としたほかは同様に操作して粒子(A1)が全面に均一に分散したシート状硬化物を得た。この硬化物をハンマーで粗粉碎し、さらにスタンプミルで微粉碎し、篩いで分別して粒径5613~10000 μ m、平均粒径6810 μ mの粒子(B9)を得た。

【0067】以下、実施例1において粒子(B1)1500g(15%)に変えて粒子(B9)1500g(15%)としたほかは同様に操作して粒子(B9)が全面的に均一に分散したシート状硬化物を得た。

【0068】得られた硬化物を実施例1と同様に処理したところ、600mm×600mm×13mmのクリアーで天然石様の石目調人工大理石が得られた。この人工大理石の破断伸度0.88%、破断強度539kgf/cm²、弾性率6.5×10⁴kgf/cm²であった。また、耐熱クラック試験の結果は、5サイクルでクラックが発生した。

【0069】〔比較例9〕実施例1と同様にして粒子(A1)を得た。ついで実施例1の粒子(B1)を得る処方において水酸化アルミニウム粉末の使用量を3700g、及び粒子(A1)の使用量を2500g(25%)としたほかは同様に操作して粒子(A1)が全面に均一に分散したシート状硬化物を得た。この硬化物をハンマーで粗粉碎し、さらにスタンプミルで微粉碎し、篩いで分別して粒径58~88 μ m、平均粒径70 μ mの粒子(B10)を得た。

【0070】ポリメタクリル酸メチル20%とメタクリル酸メチル80%からなるメタクリル酸メチルシラップ3658g、水酸化アルミニウム粉末4700g、ターシャリーブチルパーオキシマレイン酸80g、ジメタクリル酸エチレングリコール42g、粒子(B10)1500g(15重量%)を混合し、ミキサーで攪拌した。しかしながら、攪拌途中に、このスラリー状原料の粘度が上昇し、攪拌困難となるとともに、流動性を失い、型枠への注入ができなかった。

【0071】〔比較例10〕実施例1と同様にして、但し粒径208~4699 μ m、平均粒径2100 μ mの粒子(A4)を得た。ついで実施例1の粒子(B1)を得る処方において水酸化アルミニウム粉末の使用量を3700g、及び粒子(A4)の使用量を2500g(25%)としたほかは同様に操作して粒子(A4)が全面に均一に分散したシート状硬化物を得た。この硬化物をハンマーで粗粉碎し、さらにスタンプミルで微粉碎し、

篩いで分別して粒径495~10000 μ m、平均粒径3680 μ mの粒子(B11)を得た。

【0072】以下、実施例1において粒子(B1)1500g(15%)に変えて粒子(B11)1500g(15%)としたほかは同様に操作して粒子(B11)が全面的に均一に分散したシート状硬化物を得た。

【0073】得られた硬化物を実施例1と同様に処理したところ、600mm×600mm×13mmのクリアーで天然石様の石目調人工大理石が得られた。この人工大理石の破断伸度0.79%、破断強度521kgf/cm²、弾性率6.5×10⁴kgf/cm²であった。また、耐熱クラック試験の結果は、1サイクルでクラックが発生した。

【0074】〔比較例11〕ポリメタクリル酸メチル20%とメタクリル酸メチル80%からなるメタクリル酸メチルシラップ3658g、水酸化アルミニウム粉末6200g、ターシャリーブチルパーオキシマレイン酸80g、着色剤として黒ペースト50gを混合し、ミキサーで攪拌した。

【0075】この混合スラリーを真空容器中で脱泡した後、さらに、グリコールジメルカプトアセテート12g、脱イオン水8gを添加して攪拌した。このスラリーを、PVAフィルムを敷いた約60cm角の型枠中に注入し、その上からPVAフィルムを張り付けた。これを実施例1と同様にしてシート状硬化物を得た。

【0076】この硬化物をハンマーで粗粉碎し、さらにスタンプミルで微粉碎した。この粉碎工程では実施例1で得た硬化前に比較して微粒子になりにくく、所定の粒度まで粉碎するのにかなりの時間を要した。粉碎篩いで分別して粒径104~701 μ m、平均粒径340 μ mの粒子(A5)を得た。

【0077】ポリメタクリル酸メチル20%とメタクリル酸メチル80%からなるメタクリル酸メチルシラップ3658g、水酸化アルミニウム粉末3700g、ターシャリーブチルパーオキシマレイン酸80g、着色剤として白ペースト50g、粒子(A5)2500g(25重量%)を混合し、ミキサーで攪拌した。しかしながら、攪拌途中に、このスラリー状原料の粘度が上昇し、攪拌困難となるとともに、流動性を失い、型枠への注入ができなかった。

【0078】

【発明の効果】本発明の石目調人工大理石は、石目調を与える粒子中に石目調大理石を構成する組成と同様の組成の粒子を含有していることにより、石目調粒子とその周辺部分との間に物質構成に歪を起すようなことなく、従来品にない耐熱クラック性に優れたものとなっている。

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